# Metal−Metal Bond Opening Toward Main Group−Transition Element Rings

Weng Kee Leong* and Guizhu Chen

*Department of Chemistry, National University of Singapore, Kent Ridge, Singapore 119260*

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*Summary: The reaction of the cluster* $Os_6(\mu_4\text{-}Sb)(\mu\text{-}H)_2(\mu\text{-}SbPh_2)(\mu_3,\eta^2\text{-}C_6H_4)(\mu_3,\eta^4\text{-}C_{12}H_8)(CO)_{15}$, ***1****, with excess* $^tBuNC$ *resulted in ring expansion via metal−metal bond cleavage to afford the novel compounds* $Os_6(\mu_4\text{-}Sb)(\mu\text{-}H)(\mu\text{-}SbPh_2)(C_6H_5)(\mu_3,\eta^4\text{-}C_{12}H_8)(CO)_{14}(CN^tBu)_4$, ***2****, and* $Os_6(\mu_4\text{-}Sb)(\mu\text{-}H)(\mu\text{-}SbPh_2)(C_6H_5)(\mu_3,\eta^4\text{-}C_{12}H_8)(CO)_{15}(CN^tBu)_3$, ***3****, both of which contain five-membered* $Os_3Sb_2$ *rings.*

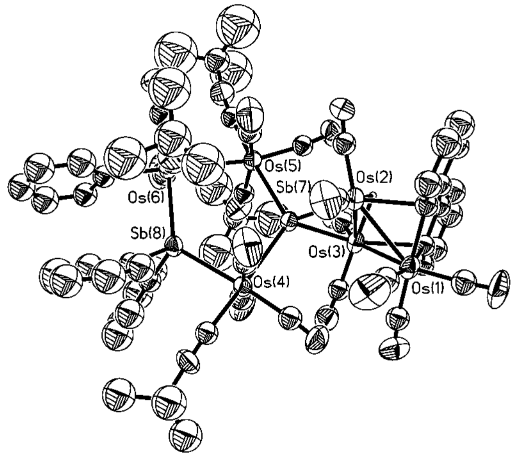

**Figure 1.** ORTEP diagram (hydrogens omitted, 50% probability thermal ellipsoids) and selected bond parameters for **2**. Os(1)Os(2) = 2.9023(8) Å, Os(1)Os(3) = 2.8932(8) Å, Os(2)Os(3) = 2.8196(8) Å, Os(5)Os(6) = 3.0294(8) Å, Os(2)Sb(7) = 2.6378(10) Å, Os(3)Sb(7) = 2.6391(10) Å, Os(4)Sb(7) = 2.7889(10) Å, Os(5)Sb(7) = 2.7283(10) Å, Os(4)Sb(8) = 2.7488(10) Å, Os(6)Sb(8) = 2.6939(11) Å, ∠Os(3)-Os(2)Sb(7) = 57.72(2)°, ∠Os(2)Os(3)Sb(7) = 57.68(3)°, ∠Os(2)Sb(7)Os(3) = 64.60(3)°, ∠Os(4)Sb(7)Os(5) = 118.84(3)°, ∠Sb(7)Os(5)Os(6) = 102.12(3)°, ∠Os(5)Os(6)Sb(8) = 94.75(3)°, ∠Os(6)Sb(8)Os(4) = 125.50(4)°, ∠Sb(8)Os(4)Sb(7) = 91.79(3)°.

Ring compounds built up of only low-valent transition metals in the ring framework are relatively uncommon; some rare examples include the puckered square $Os_4(CO)_{16}$[1] and an interesting series of four- to six-membered rhenium hydrido carbonyl rings.[2] This has been attributed to the propensity of the transition metals toward deltahedral cluster formation. One way to stabilize rings containing transition metals appears to be by the introduction of main group metals into the ring. Examples containing the smaller four-membered $E_2M_2$ (E = main group, M = transition element) ring are numerous,[3] while examples of larger ring sizes are scarce; two examples from osmium chemistry are the 12-membered-ring $[Ph_2SnOs(CO)_4]_6$, which was prepared via a salt elimination reaction between $[Os(CO)_4]^{2-}$ and $Ph_2SnCl_2$,[4] and the cluster $[Os_3(\mu\text{-}SbPh_2)(\mu\text{-}H)(CO)_{10}]_2$, which contains a six-membered $Os_4Sb_2$ ring.[5] Such reactions are predicated upon the formation of metal−metal bonds. Recently, we reported that the osmium−antimony cluster $Os_3(\mu\text{-}SbPh_2)(\mu\text{-}H)(CO)_{10}$ can undergo nucleophilic addition via metal−metal bond cleavage to form compounds with a four-membered $Os_3Sb$ ring.[6] We wish to report that a similar reaction with a more complex analogue, $Os_6(\mu_4\text{-}Sb)(\mu\text{-}H)_2(\mu\text{-}SbPh_2)(\mu_3,\eta^2\text{-}C_6H_4)(\mu_3,\eta^4\text{-}C_{12}H_8)(CO)_{15}$, **1**,[7] afforded the first examples of the five-membered $Os_3Sb_2$ ring system.

## Results and Discussion

The reaction of **1** with excess $^tBuNC$ in $CH_2Cl_2$ led to an immediate change in color from orange to red. TLC separation of the reaction mixture gave two major bands, which have been identified as the novel compounds $Os_6(\mu_4\text{-}Sb)(\mu\text{-}H)(\mu\text{-}SbPh_2)(C_6H_5)(\mu_3,\eta^4\text{-}C_{12}H_8)(CO)_{14}(CN^tBu)_4$, **2**, and $Os_6(\mu_4\text{-}Sb)(\mu\text{-}H)(\mu\text{-}SbPh_2)(C_6H_5)(\mu_3,\eta^4\text{-}C_{12}H_8)(CO)_{15}(CN^tBu)_3$, **3** (Figures 1 and 2, respectively). Immediately after addition of the $^tBuNC$, the $^1H$ NMR spectrum showed two resonances at −10.68 and −11.20 ppm in the high-field region, which were indicative of bridging hydrides. Stirring for a further 2 h showed the emergence of another resonance at −10.80 ppm. The resonances at −10.80 and −11.20 ppm have

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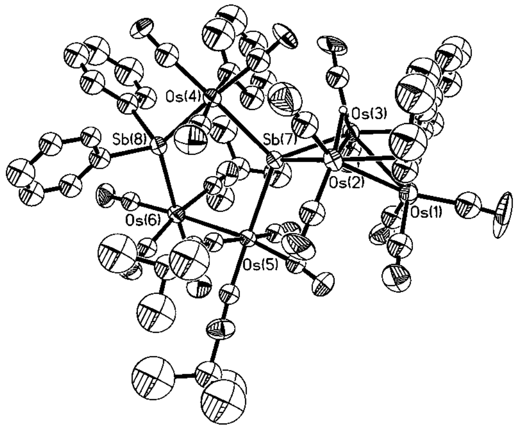


**Figure 2.** ORTEP diagram (hydrogens omitted, 50% probability thermal ellipsoids) and selected bond parameters for **3**. Os(1)Os(2) = 2.9045(12) Å, Os(1)Os(3) = 2.9322(12) Å, Os(2)Os(3) = 2.8465(11) Å, Os(5)Os(6) = 3.0452(11) Å, Os(2)Sb(7) = 2.6821(15) Å, Os(3)Sb(7) = 2.6522(14) Å, Os(4)Sb(7) = 2.7928(15) Å, Os(5)Sb(7) = 2.8002(14) Å, Os(4)Sb(8) = 2.7024(14) Å, Os(6)Sb(8) = 2.7301(15) Å, $\angle$Os(3)Os(2)Sb(7) = 57.24(3)°, $\angle$Os(2)Os(3)Sb(7) = 58.26(4)°, $\angle$Os(2)Sb(7)Os(3) = 64.50(4)°, $\angle$Os(4)Sb(7)Os(5) = 116.35(5)°, $\angle$Sb(7)Os(5)Os(6) = 100.87(4)°, $\angle$Os(5)Os(6)Sb(8) = 92.82(4)°, $\angle$Os(6)Sb(8)Os(4) = 126.88(5)°, $\angle$Sb(8)Os(4)Sb(7) = 92.05(4)°.

been assigned to **2** and **3**, respectively; the −10.68 ppm resonance could not be attributed to any of the compounds obtained after the TLC workup. Thus **3** was formed directly from the reaction, while **2** was the result of decomposition (over time and on silica gel) of the unidentified species with the −10.68 ppm resonance (Scheme 1). Antimony exhibits a greater tendency toward bridging across open metal···metal edges in comparison with the lighter congeners phosphorus and arsenic;[6] this accounts for the formation of **2** and **3** from **1** via Os−Os bond cleavage. The benzyne moiety, which was a four-electron-donor ligand in **1**, has deorthometalated to a terminal phenyl in order to accommodate the $^t$BuNC ligands.

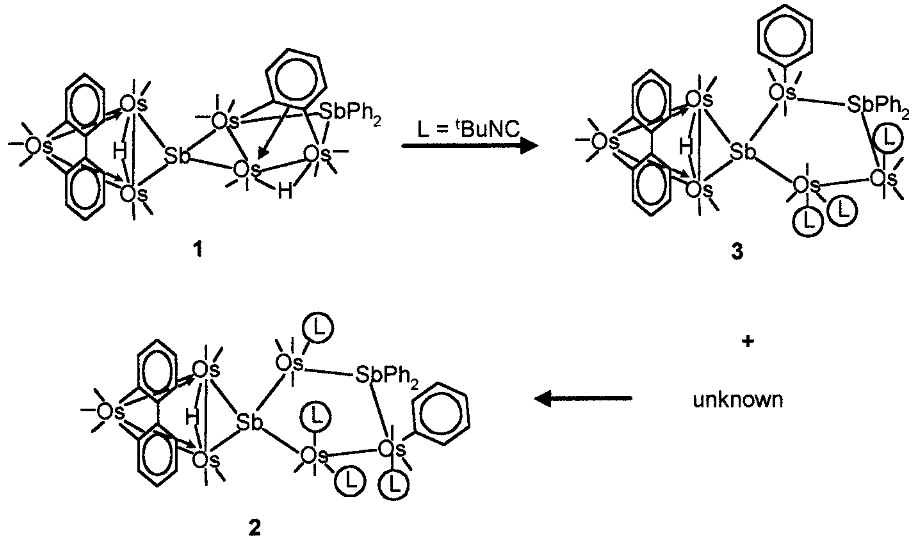
The metal cores of **2** and **3** are very similar, comprising a naked, spirocyclic antimony which is part of a five-membered $Os_3Sb_2$ ring and which also bridges a triosmium ring. The $Os_3Sb_2$ rings are puckered, more so for **2** than for **3**; the torsion angles around the Sb(7)Os(5)Os(6)Sb(8)Os(4) rings are −23.4°, −6.9°, 21.0°, −14.3°, 25.7° and −29.1°, −14.5°, 30.6°, −11.4°, 28.0°, for **2** and **3**, respectively. The main structural differences are in the ligand sets; **2** has four isocyanide ligands (two in axial and two in equatorial positions with respect to the plane of the $Os_3Sb_2$ ring) and a phenyl group on Os(6) trans to an OsOs bond, while **3** has three isocyanide ligands (one equatorial and two axial) with the phenyl group in an axial position on Os(4). As has been observed earlier for osmium−antimony clusters, the $^t$BuNC ligand did not show the usual tendency to occupy axial sites: both axial and equatorial sites were occupied.[6b] Although the antimony atoms are all four-coordinate, they are able to accommodate a large variation in bond parameters, as is demonstrated in the large variation in OsSb bond lengths (from 2.6378(10) to 2.8002(14) Å) and OsSbOs angles (from 64.50(4)° to 126.88(5)°). In contrast, the variation in angles at the osmium atoms in the $Os_3Sb_2$ rings, which have approximate octahedral geometry, tends to be comparatively more limited; the range is from 91.79(3)° to 102.12(3)°. This property of antimony is probably an important factor accounting for the formation and stability of these compounds.

The reaction reported here thus demonstrates that it is possible to construct metal rings via metal−metal bond cleavage rather than metal−metal bond formation. The scope of this methodology is currently being explored.

## Experimental Section

To a solution of **1** (30 mg, 0.014 mmol) in dichloromethane (15 mL) was added $^t$BuNC (3 drops). The color of the solution changed from orange to dark red. The mixture was stirred for another 2 h. Removal of the solvent followed by TLC separation using $CH_2Cl_2$/hexane (40:60, v/v) as eluant gave $Os_6(\mu_4\text{-}Sb)(\mu\text{-}SbPh_2)(\mu\text{-}H)(C_6H_5)(\mu_3,\eta^4\text{-}C_{12}H_8)(CO)_{14}(CNBu\mathit{t})_4$, **2** (yield = 14 mg, 42%), and $Os_6(\mu_4\text{-}Sb)(\mu\text{-}SbPh_2)(\mu\text{-}H)(C_6H_5)(\mu_3,\eta^4\text{-}C_{12}H_8)(CNBu\mathit{t})_3(CO)_{15}$, **3** (yield = 13 mg, 40%), as dark red crystalline solids. **2**: $^1$H NMR (300 MHz, $CDCl_3$, 25 °C, TMS) $\delta$ 7.8−6.4 (m; aromatic), 1.52 (s; *t*Bu), 1.33 (s; *t*Bu), 1.25 (s; *t*Bu), 1.02 (s;

**Scheme 1. Reaction Pathway from 1 to 2 and 3**



*t*Bu), −10.81 (s; OsHOs); IR ($CH_2Cl_2$) $\bar{\nu}$ 2080w, 2045m, 2016 m, 1989m, 1974s, 1943w, 1916w cm$^{-1}$ (C≡O); 2191w, 2173w, 2142w cm$^{-1}$ (C≡N). Anal. Calcd for $C_{64}H_{60}N_4O_{14}Os_6Sb_2$: C, 30.81; H, 2.41; N, 2.25. Found: C, 31.18; H, 2.79; N, 2.48. **3**: $^1$H NMR (300 MHz, $CDCl_3$, 25 °C, TMS) $\delta$ 7.8−6.5 (m, aromatic), −11.19 (s, OsHOs); IR ($CH_2Cl_2$) $\bar{\nu}$ 2058w, 2064w, 2043s, 2020m, 1997s, 1987s, 1964s, 1915m cm$^{-1}$ (C≡O); 2183w, 2168w cm$^{-1}$ (C≡N). Anal. Calcd for $C_{60}H_{51}N_3O_{15}Os_6Sb_2$: C, 29.91; H, 2.08; N, 1.89. Found: C, 29.52; H, 2.09; N, 1.72.

**Crystal Structure Determination of 2 and 3**. Crystals were obtained as dark red, thin plates from dichloromethane/hexane solutions and mounted on quartz fibers. X-ray data were collected on a Siemens SMART diffractometer, equipped with a CCD detector, using Mo Kα radiation at ambient temperature (298(2) K). Data were corrected for Lorentz and polarization effects with the SMART suite of programs,[8] and for absorption effects with SADABS.[9] Structural solution and refinement were carried out with the SHELXTL suite of programs.[10] The structures were solved by direct methods to locate the heavy atoms, followed by difference maps for the light, non-hydrogen atoms. The Os, Sb, N, and O atoms were given anisotropic thermal parameters; methyl carbons in each $^t$Bu group were given the same isotropic thermal parameters. Organic hydrogens were placed in calculated positions and given an isotropic thermal parameter 1.1 times that of the carbon atoms they are attached to and riding on them. Metal hydrides were placed in positions calculated with XHYDEX[11] and refined with a fixed isotropic thermal parameter of 0.05 Å$^2$ and riding on one of the osmium atoms that it is bonded to. All phenyl rings were regularized. The following groups of bond lengths in **2** were restrained to be equal: C≡O, C≡N, and C−$CH_3$. Refinements were against $|F^2|$.

**Crystal data for 2**: triclinic, $P\bar{1}$; $a$ = 14.7057(6) Å, $b$ = 14.9592(6) Å, $c$ = 19.3658(7) Å, α = 74.130(1)°, $\beta$ = 79.315(1)°, $\gamma$ = 81.980(1)°; $V$ = 4009.0(3) Å$^3$; $Z$ = 2, $\rho_{calcd}$ = 2.066 g/cm$^3$; 2$\theta_{max}$ = 29.29°; 28 011 reflections measured, all 18 688 independent reflections ($R_{merge}$ = 0.0344) used in refinement; $\mu$ = 10.184 mm$^{-1}$, transmission range = 0.279979−0.135917; R1 = 0.0654, wR2 = 0.1681 ($I > 2\sigma(I)$); R1 = 0.1017, wR2 = 0.1943 (all data); largest difference peak = 3.56 e Å$^{-3}$ at 0.94 Å from Os(4).

**Crystal data for 3**: monoclinic, $P2_1/n$; $a$ = 12.7872(1) Å, $b$ = 33.8780(3) Å, $c$ = 16.7793(2) Å, $\beta$ = 93.050(1)°; $V$ = 7258.58(12) Å$^3$; $Z$ = 4, $\rho_{calcd}$ = 2.232 g/cm$^3$; 2$\theta_{max}$ = 29.18°; 46 110 reflections measured, all 17 594 independent reflections ($R_{merge}$ = 0.1418) used in refinement; $\mu$ = 11.248 mm$^{-1}$, transmission range = 0.357108−0.084354; R1 = 0.0771, wR2 = 0.1835 ($I > 2\sigma(I)$); R1 = 0.1699, wR2 = 0.2162 (all data); largest difference peak = 2.94 e Å$^{-3}$ at 0.99 Å from Os(6).

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-166134 and CCDC-166135. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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**Supporting Information Available:** Crystallographic data for **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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